SACRED HEART MATRICULATION HIGHER SECONDARY SCHOOL

COMMON HALF YEARLY EXAM – DECEMBER 2022

STD: **12**
CHEMISTRY ANSWERKEY

TIME: **180 MINUTES** MAXIMUM MARKS: **70**

PART – A

I. ***Answer all the questions. Choose the correct answer from the given four alternatives and write the option code and the corresponding answer.*** **(15x1=15)**

1. a) Lower the melting point of alumina
2. a) $_5B^{10}$
3. a) H_3PO_3
4. c) 52.67
5. d) Potassium trioxalato aluminate (III)
6. c) 32%
7. c) 2.305 K J mol^{-1}
8. b) 5.55×10^{-10}
9. c) Porus graphite
10. a) A-(4), B-(1), C-(2), D-(3)
11. b) S_N^2 reaction
12. b) Cannizaro reaction
13. b) 2,4 – dimethyl aniline
14. c) Pantothanic acid
15. d) They contain strong covalent bonds in their polymer chains

PART – B

II. ***Answer any six questions. Question No.17 is compulsory.*** **(7x2=14)**

16. Give the limitation of Ellingham diagram.

- Ellingham diagram is constructed based only on thermodynamic considerations.
- It does not tell anything about the rate of the reaction.
- The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the products which is not always true.

17. What is inert pair effect?

In heavier post transition metals, the outer ***s*** electrons (***ns***) have a tendency to remain inert and show reluctance as inert pair effect.

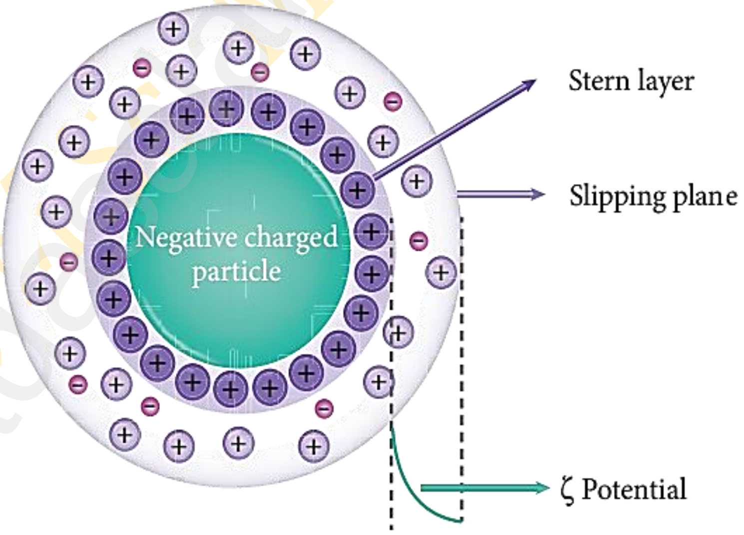
18. What is crystal field splitting energy?

- The orbitals lying along the axes dx^2-y^2 and dz^2 orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and d_{zx}). Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.
- In an octahedral complex, the d – orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy.

19. Differentiate crystalline solids and amorphous solids?

S.no	Crystalline solids	Amorphous solids
1	Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
2	Definite shape	Irregular shape
3	Generally crystalline solids are anisotropic in nature	They are isotropic* like liquids
4	They are true solids	They are considered as pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded.
7	Examples: NaCl , diamond etc.,	Examples: Rubber , plastics, glass etc

20. Explain Helmholtz double layer.

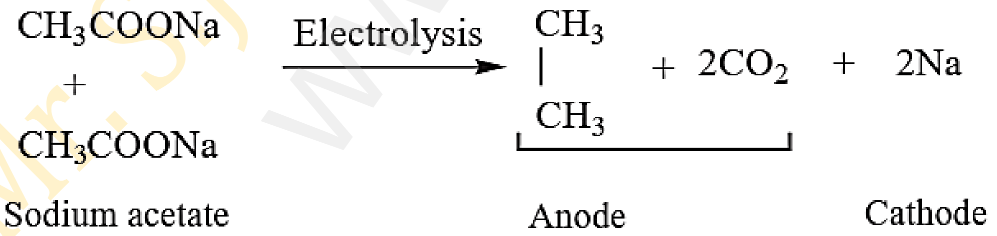


The surface of colloidal particle adsorbs one type of ion due to preferential adsorption. This layer attracts the oppositely charged ions in the medium and hence at the boundary separating the two electrical double layers are setup. This is called as Helmholtz electrical double layer.

As the particles nearby are having similar charges, they cannot come close and condense. Hence this helps to explain the stability of a colloid.

21. Explain Kolbe's electrolytic reaction.

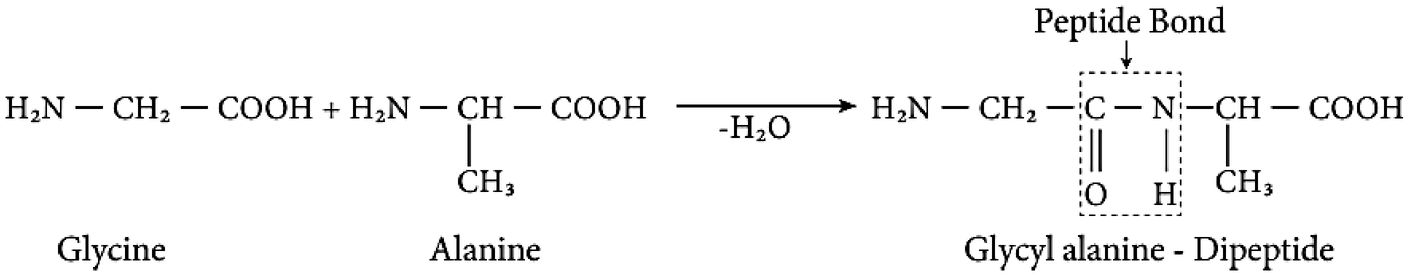
The aqueous solutions of sodium or potassium salts of carboxylic acid on electrolysis gives alkanes at anode. This reaction is called kolbes electrolysis.



$$\underset{\text{Sodium acetate}}{\begin{matrix} CH_3COONa \\ + \\ CH_3COONa \end{matrix}} \xrightarrow{\text{Electrolysis}} \underbrace{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2CO_2}_{\text{Anode}} + \underset{\text{Cathode}}{2Na}$$

22. Write a short note on peptide bond.

- The amino acids are linked covalently by peptide bonds.
- The carboxyl group of the first amino acid react with the amino group of the second amino acid to give an amide linkage between these amino acids.
- This amide linkage is called peptide bond. The resulting compound is called a dipeptide.
- If the number of amino acids are less it is called as a polypeptide, if it has large number of amino acids (and preferably has a function) then it is called a protein.



$$H_2N-CH_2-COOH + H_2N-\underset{\underset{CH_3}{|}}{CH}-COOH \xrightarrow[-H_2O]{} H_2N-CH_2-\underset{\underset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{CH_3}{|}}{CH}-COOH$$

23. Write a note on vulcanization of rubber.

- The process of mixing natural rubber with sulphur is called vulcanization.
- Natural rubber is mixed with 3-5% sulphur and heated at 100-150°C causes cross linking of the cis-1,4-polyisoprene chains through disulphide (-S-S-) bonds.
- The physical properties of rubber can be altered by controlling the amount of sulphur that is used for vulcanization.
- In sulphur rubber, made with about 1 to 3% sulphur is soft and stretchy.
- When 3 to 10% sulphur is used the resultant rubber is somewhat harder but flexible.

24. Calculate the electro chemical equivalent of silver in silver nitrate.

$$\text{Electrochemical equivalent of } M^{n+} = \frac{\text{Molarmass of M}}{\text{n (96500)}}$$

$$Z = \frac{\text{molarmass of Ag}}{(96500)} = \frac{108}{1\times96500} \qquad = 1.12\text{x}10^{-3}\ gC^{-1}$$

PART – C

III. ***Answer any six questions. Question No.32 is compulsory.*** **(6x3=18)**

25. Give the uses of Silicones.

- Silicones are used for low temperature lubrication and in vacuum pumps, high temperature oil baths etc...
- They are used for making water proofing clothes
- They are used as insulting material in electrical motor and other appliances
- They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

26. How will you identify borate radical?

- When boric acid or borate salt is heated with ethyl alcohol in presence of conc. Sulphuric acid, an ester, tri ethyl borate is formed.
- The vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow[H_2SO_4]{\text{Conc.}} B(OC_2H_5)_3 + 3H_2O$$

27. How is pure phosphine prepared from phosphorous acid?

Phosphine is prepared in pure form by heating phosphorous acid.

$$\underset{\text{Phosphorous acid}}{4H_3PO_3} \xrightarrow{\Delta} \underset{\text{Ortho phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3\uparrow}$$

A pure sample of phosphine is prepared by heating phosphonium iodide with caustic soda solution.

$$PH_4I + NaOH \xrightarrow{\Delta} \underset{\text{Phosphine}}{PH_3\uparrow} + NaI + H_2O$$

28. Write the differences between order and molecularity of a reaction?

S.No.	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
3	It is assigned for a overall reaction.	It is assigned for each elementary step of mechanism.

29. Discuss the Lowry – Bronsted concept of acids and bases.

Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus, HCl behaves as an acid and H_2O is base. The proton transfer from the acid to base can be represented as

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

When ammonia is dissolved in water, it accepts a proton from water. In this case, ammonia (NH_3) acts as a base and H_2O is acid. The reaction is represented as

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

Let us consider the reverse reaction in the following equilibrium

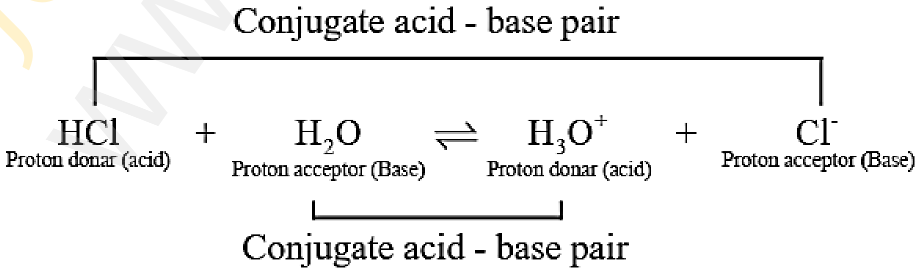
$$\underset{\text{Proton donar (acid)}}{HCl} + \underset{\text{Proton acceptor (Base)}}{H_2O} \rightleftharpoons \underset{\text{Proton donar (acid)}}{H_3O^+} + \underset{\text{Proton acceptor (Base)}}{Cl^-}$$

H_3O^+ donates a proton to Cl^- to form HCl i.e., the products also behave as acid and base.

In general, Lowry – Bronsted (acid – base) reaction is represented as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

The species that remains after the donation of a proton is a base (Base 1) and is called the conjugate base of the Bronsted acid (Acid 1). In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.



HCl and Cl^-, H_2O and H_3O^+ are two conjugate acid – base pairs. i.e., Cl^- is the conjugate base of the acid HCl. (or) HCl is conjugate acid of Cl^-. Similarly H_3O^+ is the conjugate acid of H_2O.

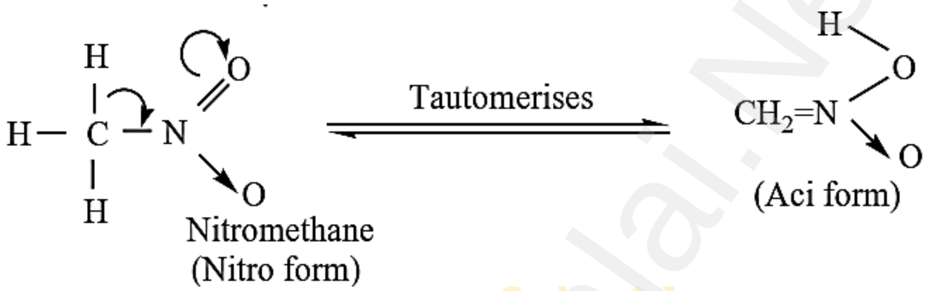
30. Explain the factors affecting electrolytic conductance?

If the interionic attraction between the oppositely charged ions of solutes increases, the conductance will decrease.

- Solvent of higher dielectric constant show high conductance in solution.
- Conductance is inversely proportional to the Viscosity of the medium. i.e., conductivity increases with the decrease in viscosity.
- If the temperature of the electrolytic solution increases, conductance also increases. Increase in temperature increases the kinetic energy of the ions and decreases the attractive force between the oppositely charged ions and hence conductivity increases.
- Molar conductance of a solution increases with increase in dilution. This is because, for a strong electrolyte, interionic forces of attraction decrease with dilution. For a weak electrolyte, degree of dissociation increases with dilution.

31. Explain Tautomerism.

Primary and secondary nitroalkanes, having α-H , also show an equilibrium mixture of two tautomers namely nitro – and aci – form



32. How is Teflon prepared?

The monomer is tetrafluroethylene. When the monomer is heated with oxygen (or) ammonium persulphate under high pressure, Teflon is obtained.

$$n\,CF_2=CF_2 \xrightarrow{\Delta} -\!\!(CF_2-CF_2)\!\!-_n$$

It is used for coating articles and preparing non – stick utensils.

33. Identify A, B and C Ethanoic acid $\xrightarrow{SOCl2}$ A $\xrightarrow{Pd\ /\ BaSO4}$ B $\xrightarrow{NaOH}$ C

A → CH_3COCl **B** → CH_3CHO **C** → $CH_3CH(OH)CH_2CHO$ ***(Aldol)***

PART – D

IV. ***Answer all the questions.*** **(5x5=25)**

34. (a) (i) Describe a method for refining Nickel.

The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$$Ni\ (s) + 4\ CO\ (g) \longrightarrow [Ni(CO)_4]\ (g)$$

On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.

$$[Ni(CO)_4]\ (g) \longrightarrow Ni\ (s) + 4\ CO\ (g)$$

(ii) What is Auto reduction?

Simple roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting of its ore cinnabar (HgS)

$$HgS\ (s) + O_2\ (g) \longrightarrow Hg\ (l) + SO_2\uparrow$$

(OR)

(b) (i) Complete the following reactions.

A) $H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$

B) $B(OH)_3 + NH_3 \longrightarrow BN + 3H_2O$

(ii) Write about Holmes signal.

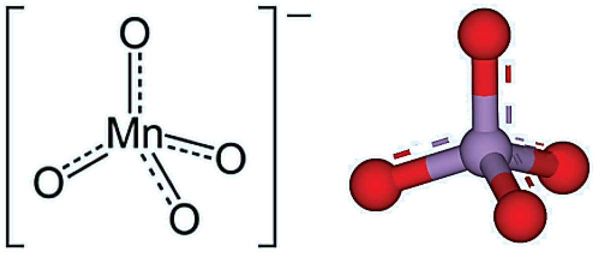
Phosphine is used for producing smoke screen as it gives large smoke. In a ship, a pierced container with a mixture of calcium carbide and calcium phosphide, liberates phosphine and acetylene when thrown into sea. The liberated phosphine catches fire and ignites acetylene. These burning gases serves as a signal to the approaching ships. This is known as **Holmes signal**.

35.(a) (i) Compare Lanthanoides and Actinoides

s.no	Lanthanoids	Actinoids
1	Differentiating electron enters in 4f orbital	Differentiating electron eneters in 5f orbital
2	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3	They show less tendency to form complexes	They show greater tendency to form complexes
4	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For example. U^{3+} (red), U^{4+} (green) , UO_2^{2+} (yellow)
5	They do not form oxo cations	They do form oxo cations such as UO_2^{2+}, NpO_2^{2+} etc
6	Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7.

(ii) Explain the structure of permanganate ion.

Permanganate ion has tetrahedral geometry in which the central Mn^{7+} is sp^3 hybridised.



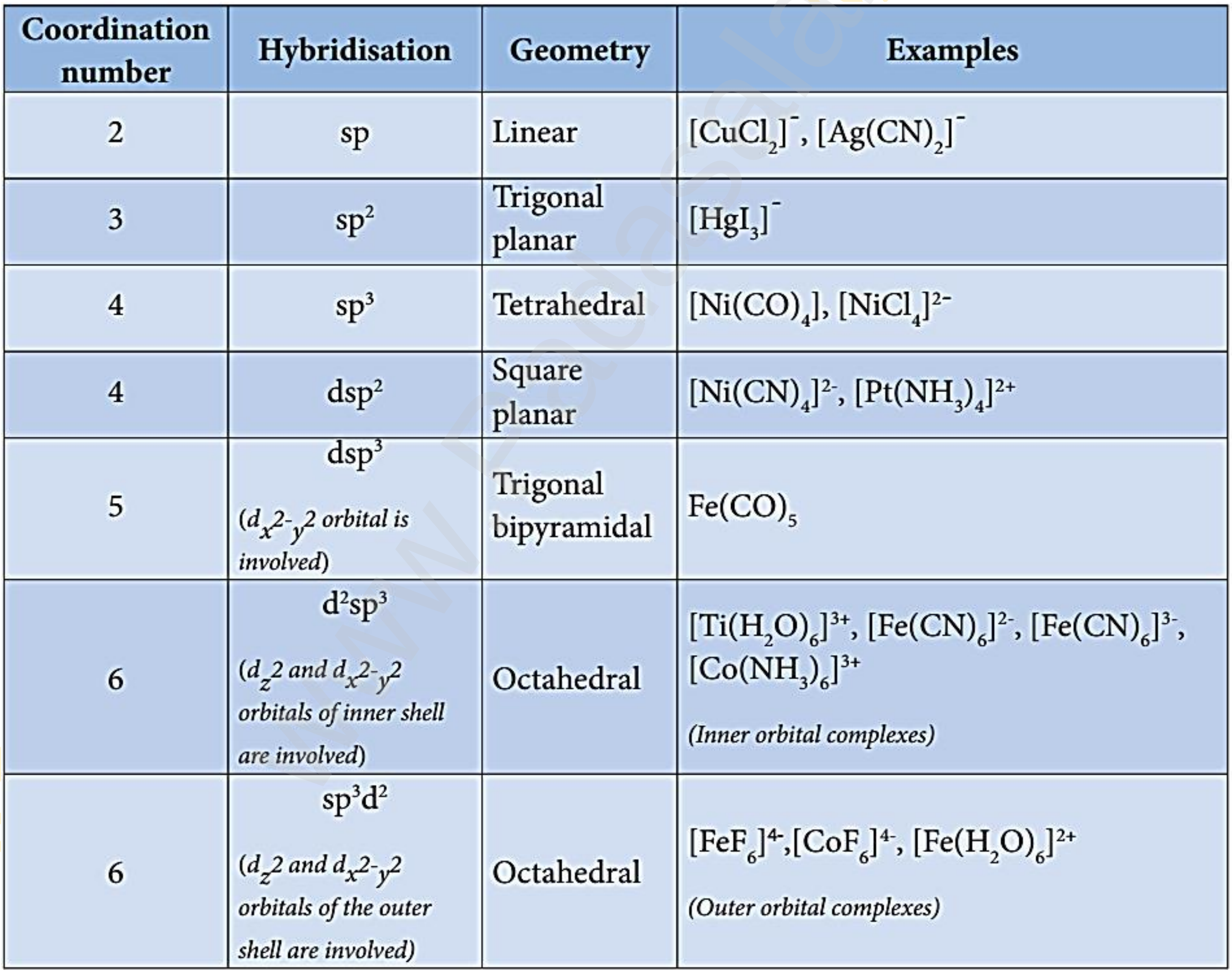
(OR)

(b) Write the postulates of valence bond theory.

According to this theory, the bond formed between the central metal atom and the ligand is due to the overlap of filled ligand orbitals containing a lone pair of electron with the vacant hybrid orbitals of the central metal atom.

Main postulates of VBT:

- The ligand → metal bond in a coordination complex is covalent in nature. It is formed by sharing of electrons (provided by the ligands) between the central metal atom and the ligand.
- Each ligand should have at least one filled orbital containing a lone pair of electrons.
- In order to accommodate the electron pairs donated by the ligands, the central metal ion present in a complex provides required number (coordination number) of vacant orbitals.
- These vacant orbitals of central metal atom undergo hybridisation, the process of mixing of atomic orbitals of comparable energy to form equal number of new orbitals called hybridised orbitals with same energy.
- The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.
- The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.



Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[CuCl_2]^-$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiCl_4]^{2-}$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	dsp^3 *($d_{x^2-y^2}$ orbital is involved)*	Trigonal bipyramidal	$Fe(CO)_5$
6	d^2sp^3 *(d_{z^2} and $d_{x^2-y^2}$ orbitals of inner shell are involved)*	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ *(Inner orbital complexes)*
6	sp^3d^2 *(d_{z^2} and $d_{x^2-y^2}$ orbitals of the outer shell are involved)*	Octahedral	$[FeF_6]^{4-}$,$[CoF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ *(Outer orbital complexes)*

- In the octahedral complexes, if the (n-1) d orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the nd orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principal quantum number of the outermost shell.

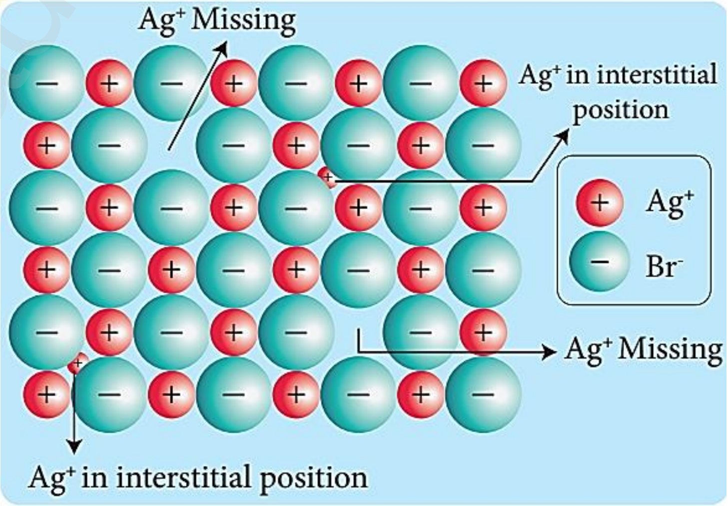
- The complexes containing a central metal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes will be diamagnetic.
- Ligands such as CO, CN^-, en, and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.
- Greater the overlapping between the ligand orbitals and the hybridised metal orbital, greater is the bond strength.

36.(a) (i) Distinguish between tetrahedral and octahedral voids.

Tetrahedral voids	**Octahedral voids**
When a sphere of second layer (b) is above the void (x) of the first layer (a), tetrahedral void is formed.	When the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), octahedral void is formed.
If the number of close packed sphere be 'n' then, the number of tetrahedral voids generated is equal to 2n.	If the number of close packed sphere be 'n' then, the number of octahedral voids generated is equal to n.
This constitutes four spheres, three on the lower (a) and one in the upper layer (b)	This constitutes six spheres, three on the lower (a) and three in the upper layer (b)
When the centres of these four spheres are joined, a tetrahedron is formed.	When the centres of these six spheres are joined, a octahedron is formed.
The coordination number is 4.	The coordination number is 6.

(ii) Explain Frenkel defect

- Frenkel defect arises due to the dislocation of ions from its crystal lattice.
- The ion which is missing from the lattice point occupies an interstitial position.
- This defect is shown by ionic solids in which cation and anion differ in size. Unlike Schottky defect, this defect does not affect the density of the crystal.



- For example AgBr, in this case, small Ag^+ ion leaves its normal site and occupies an interstitial position.

(OR)

(b) Derive Integrated rate law for the first order reaction.

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following first order reaction,

$$A \longrightarrow \text{product}$$

Rate law can be expressed as

$$\text{Rate} = k\,[A]^1$$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k\,[A]^1$$

$$\Rightarrow \frac{-d[A]}{[A]} = k\,dt$$

Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration $[A_0]$ to [A] at the later time.

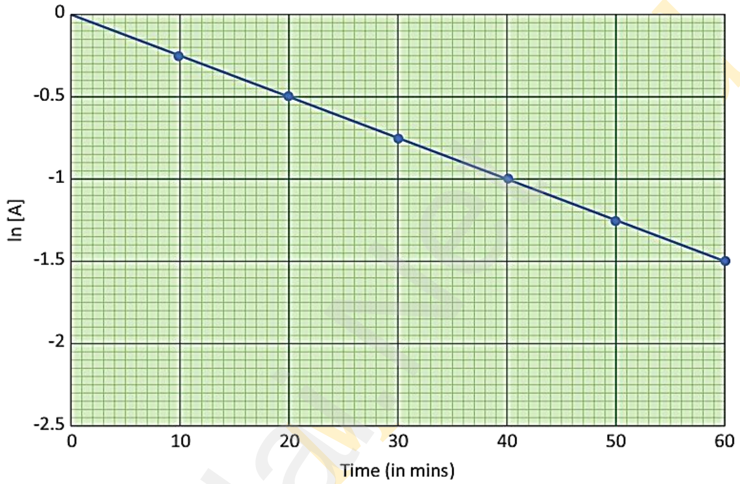
$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k\int_0^t dt$$

$$\left(-\ln[A]\right)_{[A_0]}^{[A]} = k\left(t\right)_0^t$$

$$-\ln[A] - \left(-\ln[A_0]\right) = k\,(t-0)$$

$$-\ln[A] + \ln[A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt$$



This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$$2.303\log\left(\frac{[A_0]}{[A]}\right) = kt$$

$$k = \frac{2.303}{t}\log\left(\frac{[A_0]}{[A]}\right)$$

Equation (2) can be written in the form y = mx + c as below

$$\ln[A_0] - \ln[A] = kt$$

$$\ln[A] = \ln[A_0] - kt$$

$$\Rightarrow y = c + mx$$

If we follow the reaction by measuring the concentration of the reactants at regular time interval't', a plot of ln[A] against 't' yields a straight line with a negative slope. From this, the rate constant is calculated.

37.(a) (i) Derive an expression for Ostwald's Dilution Law.

The dissociation of acetic acid can be represented as

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

The dissociation constant of acetic acid is,

$$k_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of dissociation of CH_3COOH	α	-	-
Number of moles at equilibrium	$1-\alpha$	α	α
Equilibrium concentration	$(1-\alpha)C$	αC	αC

Substituting the equilibrium concentration in equation

$$k_a = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C}$$

$$k_a = \frac{\alpha^2 C}{1-\alpha}$$

We know that weak acid dissociates only to a very small extent. Compared to one, α is so small and hence in the denominator $(1 - \alpha) \approx 1$. The above expression now becomes,

$$K_a = \alpha^2 C$$

$$\Rightarrow \alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

(ii) **Is it possible to store copper sulphate in an iron vessel for a long time?**

Given: $E^o_{Cu2-/Cu} = 0.34V$ and $E^o_{Fe2+/Fe} = 0.44V$

$$\left(E^o_{ox}\right)_{Fe|Fe^{2+}} = 0.44V \text{ and } \left(E^o_{red}\right)_{Cu^{2+}|Cu} = 0.34V$$

These +ve emf values shows that iron will oxidise and copper will get reduced i.e., the vessel will dissolve. Hence it is not possible to store copper sulphate in an iron vessel.

(OR)

(b) **What are the characteristics of a catalyst.**

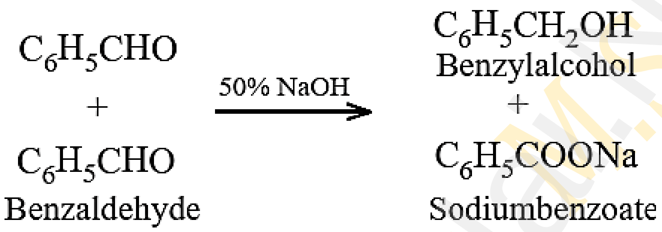
- For a chemical reaction, catalyst is needed in very small quantity. Generally, a pinch of catalyst is enough for a reaction in bulk.
- There may be some physical changes, but the catalyst remains unchanged in mass and chemical composition in a chemical reaction.
- A catalyst itself cannot initiate a reaction. It means it can not start a reaction which is not taking place. But, if the reaction is taking place in a slow rate it can increase its rate.
- A solid catalyst will be more effective if it is taken in a finely divided form.
- A catalyst can catalyse a particular type of reaction, hence they are said to be specific in nature.
- In an equilibrium reaction, presence of catalyst reduces the time for attainment of equilibrium and hence it does not affect the position of equilibrium and the value of equilibrium constant.

- A catalyst is highly effective at a particular temperature called as optimum temperature.
- Presence of a catalyst generally does not change the nature of products
  For example. $2SO_2 + 2O_2 \rightarrow SO_3$
- This reaction is slow in the absence of a catalyst, but fast in the presence of Pt catalyst

38.(a) Explain the mechanism of cannizaro reaction.

In the presence of concentrated aqueous or alcoholic alkali, aldehydes which do not have α - hydrogen atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and a salt of carboxylic acid. This reaction is called Cannizaro reaction.

Benzaldehyde on treatment with concentrated NaOH (50%) gives benzyl alcohol and sodium benzoate.

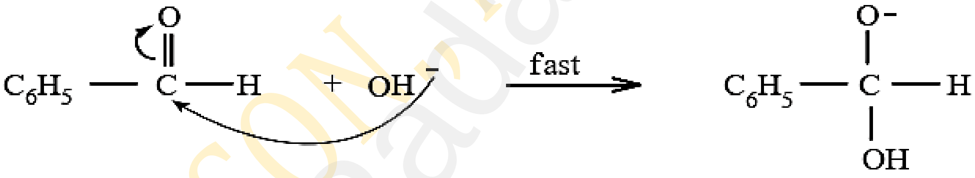


This reaction is an example disproportionation reaction

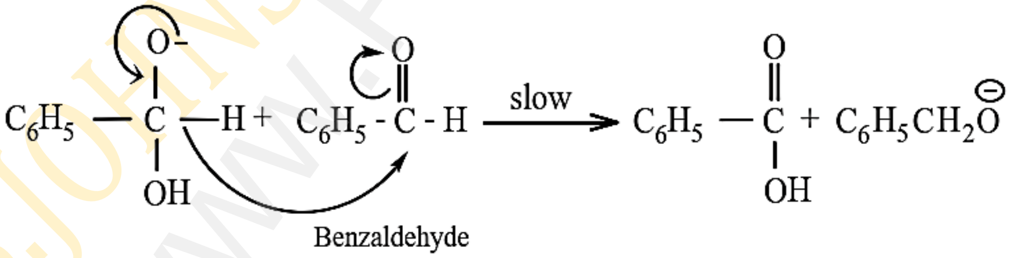
Mechanism of Cannizaro reaction

Cannizaro reaction involves three steps.

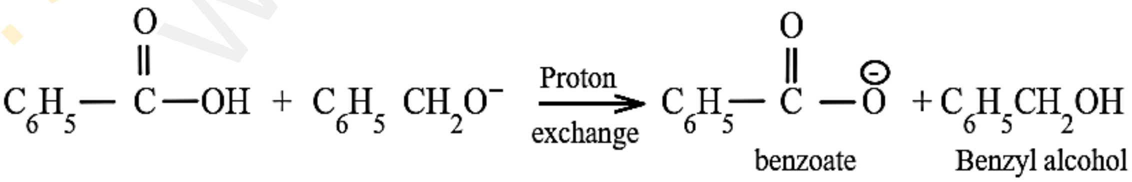
Step 1: Attack of OH- on the carbonyl carbon.



Step 2: Hydride ion transfer



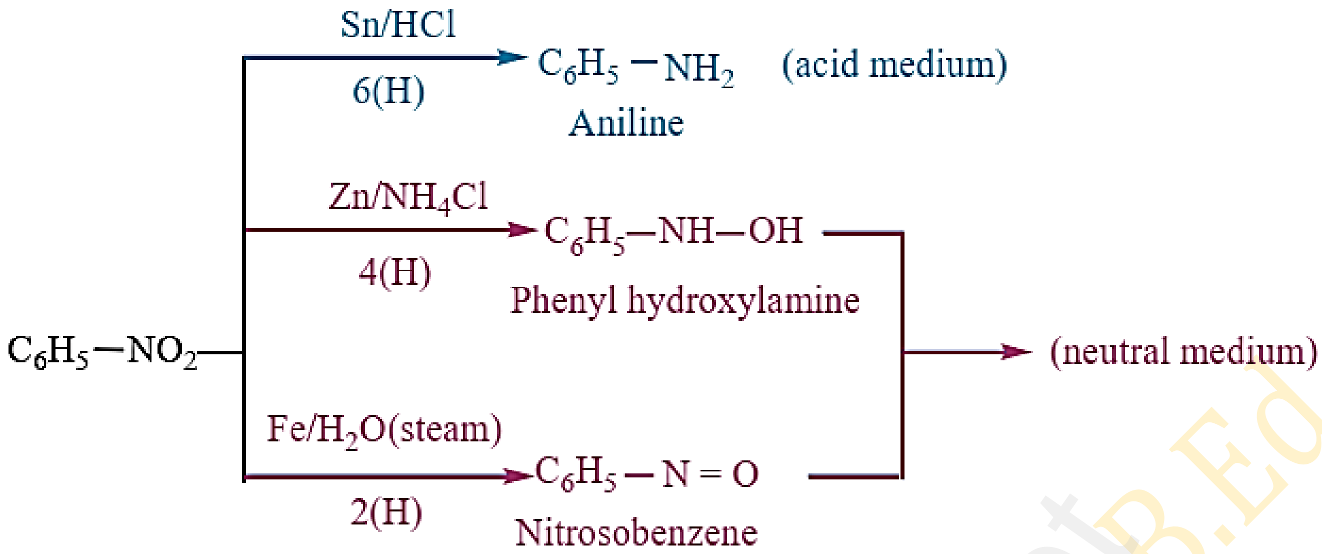
Step 3: Acid – base reaction.



Cannizaro reaction is a characteristic of aldehyde having no α – hydrogen.

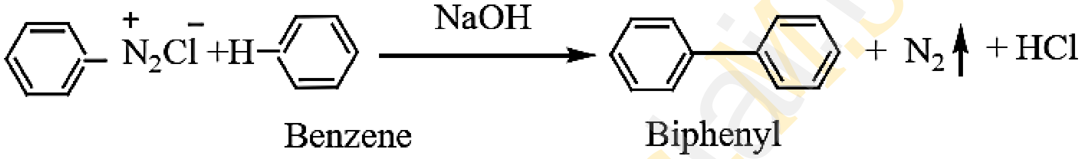
(OR)

(b) (i) Write the reduction products are obtained when nitrobenzene is reduced in acid medium and neutral medium.



(ii) Write short notes on Gomberg reaction.

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.



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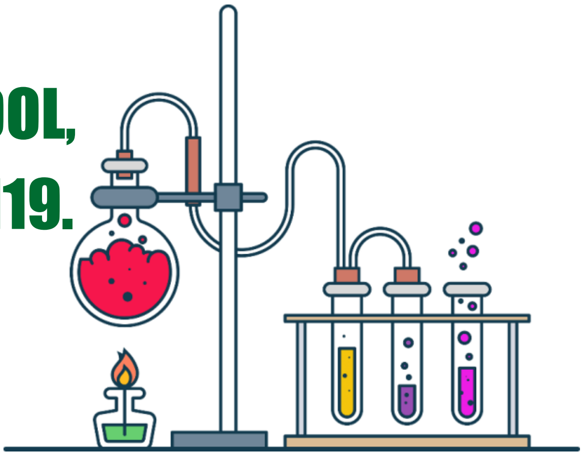

Happy Christmas &
Happy New Year 2023